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Novel Dysprosium and Terbium Doped Taggants for Hydrocarbon Identification

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ABSTRACT

Taggants are synthesized fluorescent materials that have longer lifetime and are able to discriminate against background interference arising from hydrocarbons. Doped taggants were prepared with dysprosium and terbium rare earths in a stable borosilicate and tellurite glass host. The composition of the doped borosilicate glass were (60-x) ZnO + 20B_2O_3 + 20SiO_2 + xLa^{3+} (where La^{3+} = Tb and Dy), while the composition of doped tellurite glass composition was (80-x) TeO_2 + 20$LiCO_3$ + xLa^{3+} (where La^{3+} = Tb and Dy) with values of x corresponding to mol% increase from 0.5, 1.0, 1.5, and 2.0 and subsequent decrease of ZnO and TeO_2 composition. The fluorescence emissions of dysprosium doped borosilicate and tellurite glass was 574 nm while Terbium doped borosilicate and tellurite glasses at 544 nm. The UV/Vis absorption characterization showed dysprosium doped borosilicate glass as having the strongest absorption spectra with several excitation peaks and maximum absorption (λmax) at 350 nm while fluorescence compatibility test for cyclohexane and crude oil identified Dysprosium borosilicate glass and terbium tellurite glass as the optimum taggants showing compatibility with the hydrocarbons.

1. Introduction

Different sources of hydrocarbons are difficult to identify because the same compound could be formed under various conditions [1]. For e.g. triterpanes and steranes are particularly suitable for source identification of petroleum residues in coastal sediments while acyclic isoprenoids, terpanes and steranes are suggested as passive tags for source recognition of oil spills by mass fragmentography [2]. Also a study using cyclic terpenoid biomarker fingerprints of refined oil and motor oils used to identify the origin and presence of diffuse lubricating oil contamination in sediments showed that the disparity in the relative abundance of petroleum biomarkers in different environmental samples were related to the relative contribution of different oil sources with distinct biomarker profiles and to the degree of weathering [3].

Research has identified glass host as a good environmental tracer since it protects the dopants from water quenching external influences and degradation and also observed that doped borosilicate glass and lanthanide chelate doped polymer spheres had significant narrower bandwidth emission peaks and achieved more selective detection of multiple tracers without overlap [4]. In addition, research on neodymium type doped telluride-tungsten glass [5] confirmed that the average emission across each section of the doped glass, determined from a lasing threshold data, was in good agreement with values obtained from the spectroscopic analysis based on Judd-Ofelt theories of rare earths [6]. Moreover mixtures of lanthanides will not disproportionate and enabling the possibility of devising tagging scheme based on the concentration of a number of rare earths relative to a particular rare earth likewise their oxides give unique narrow band absorption and emission properties which are not observed in fluorescent dyes [7]. Notably, the significance of ZnO-B_2O_3-SiO_2 glass host doped with neodymium (Nd^{3+}) was demonstrated in a Near Infrared Radiation (NIR) emission experiment [8], the profiles obtained demonstrated its suitability not only as a rich NIR luminescent at 1.06 µm but also as an important violet up-converted phenomena with potential applications. Another study examined the absorption and fluorescence of Eu^{3+} ions doped in a given telluride glass matrix [9] and demonstrated that telluride glass matrix has potential for a good laser material at 613.6 nm due to $5D_0$-$7F_2$ transitions given low phonon vibrations compared to other oxide and phosphate glasses hence the fluorescence of the marker is detected after the interfering sources of fluorescence have ceased; the taggant thus acts as tracers [10-12]. Therefore this study will investigate the fluorescence potentials of synthesized dysprosium and terbium doped glass taggants for identification of hydrocarbon.

2. Experimental Methods

Sigma Aldrich chemicals were used and includes zinc oxide, silicon dioxide, terbium III chloride hexahydrate and dysprosium III chloride hexahydrate all of 99.9% purity while boron oxide, tellurium dioxide, lithium carbonate and cyclohexane were of 99% purity and crude oil sample from NALCO Britannia platform, Aberdeen, Scotland.

2.1 Zinc Borosilicate Glass Synthesis

The synthesis of zinc borosilicate glass was 60ZnO + 20B_2O_3 + 20SiO_2, (Mol%). The batches of the chemical mix weighed were weighed accordingly totaling 7 g as follows: ZnO = 4.5717 g, B_2O_3 = 1.3034 g, SiO_2 = 1.1253 g. The batch mixture of doped borosilicate glass was calculated at (60-x) ZnO + 20B_2O_3 + 20SiO_2 + xLa^{3+} (where La^{3+} = Tb and Dy), and values of x relates to decrease of ZnO composition and corresponding mol% increase from 0.5, 1.0, 1.5, and 2.0.

2.2 Tellurite Glass Synthesis

The chemical composition of tellurite glass was 80TeO_2 + 20$LiCO_3$, (Mol%) while the batch of the chemical mix were equivalently at 7 g and weighed out as follows, TeO_2 = 6.2741 g, $LiCO_3$ = 0.1037 g. The composition of doped tellurite glass composition was calculated at (80-x) TeO_2 + 20$LiCO_3$ + xLa^{3+} (where La^{3+} = Tb and Dy) and values of x corresponding to an increase in mol% from 0.5, 1.0, 1.5, 2.0 with equivalent decrease in of TeO_2 composition.

2.3 Batch Preparation

Each single glass batch mixture was weighed into agate ball mill and then ball milled for 3 minutes in order to obtain a homogeneous mixture before been transferred to a platinum crucible. The platinum crucible was introduced into 1600 Carbolite high temperature furnace at a controlled temperature program from 4000 °C to 8000 °C for tellurite batches and 400 to 1600 °C for zinc borosilicate batches. Then the glass melt poured

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into the hot plate brass mould already at annealing temperature of 1500 °C reducing cracking of the glass [12, 13].

2.4 Stock Solution Preparation

100 ppm stock solution of crude oil was prepared by measuring; 0.5 mL of crude oil was into 50 mL cyclohexane. 10 ppm prepared by a 10 x dilution in cyclohexane.

2.5 Instrumentation

The blank samples (borosilicate glass and tellurite glass) and doped glass samples (terbium and dysprosium doped borosilicate glass and tellurite glass) were each characterized using Perkin Elmer Lambda 900 UV/Vis and Perkin Elmer LS50B fluorescence spectrometer. The UV/Vis absorption maxima of cyclohexane was at 261 nm and crude oil at 219 nm while characterization by fluorescence spectrometer determined the emission wavelength of cyclohexane to be 523 nm and crude oil at 350 nm respectively [14].

3. Results and Discussion

3.1 Absorption Determination

The glass samples showed that the terbium doped borosilicate glass (TBSG) had absorption maxima at 350 nm and 483 nm while the terbium doped tellurite glass (TTEG) had its absorption maxima at only 484 nm. The dysprosium doped borosilicate glass (DBSG) had absorption maxima at 349 nm and 452 nm while the dysprosium doped tellurite glass (DTEG) was observed to be 451 nm and 481 nm respectively as; new forms of molecular interaction but not within the scope of the project. For crude oil characterization DBSG was scanned at 349 nm and 452 nm excitation wavelengths, DTEG scanned at 453 nm and 481 nm excitation wavelengths, TBSG scanned at 350 nm and 483 nm excitation wavelengths while TTEG scanned only at excitation wavelength of 484 nm [15].

3.2 UV/Vis and Fluorescence Analysis

The blanks of the undoped borosilicate glass and tellurite glass had no aborption and were used as control samples and shown in Fig. 1 below.

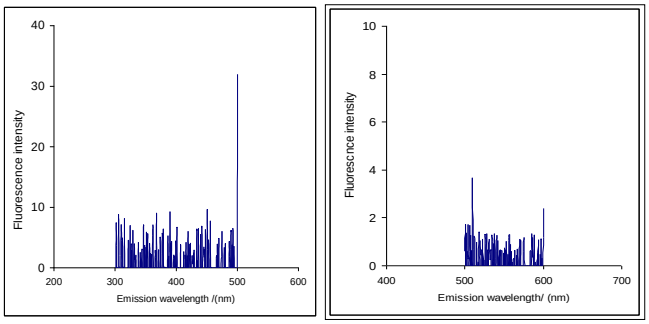

Fig. 1 Typical excitation and emission of blank samples

The characterization of the samples were performed and determined. The excitation wavelength of DBSG with absorption maxima of 349 nm and 452 nm is at the RHS while TBSG with absorption maxima of 350 nm and 483 nm is on LHS in Fig. 2 below.

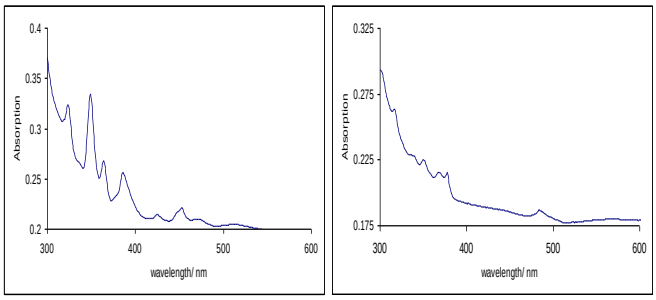

Fig. 2 Graph of 2 mol% DBSG (LHS) and 2 mol% TBSG UV/VIS absorption wavelength

Also shown in Fig. 3 on the LHS is TTEG showing only one peak at 484 nm while on the RHS is DTEG showing its two absorption maxima at 453 nm and 481 nm respectively.

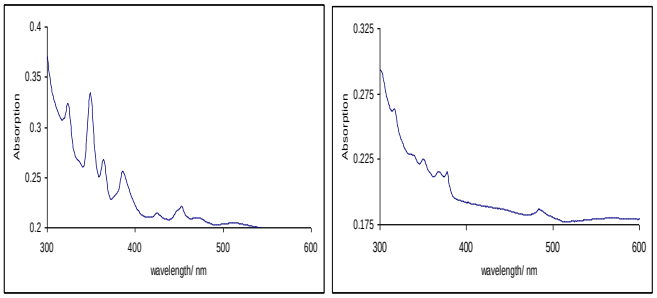

Fig. 3 2 mol% TBTEG (LHS) and 2 mol% DTEG (RHS) UV/VIS absorption spectrum

DBSG and TBSG in contrast to TTEG and DTEG had absorption maxima within the UV/VIS wavelength range showing enhanced light absorption from borosilicate glass host. Also excitation wavelength values were used to obtain emission wavelegths from flourescence analyses (Fig. 4). Single emission scans to determine their emission wavelength demonstrated that irrespective of their glass host and corresponding concentrations DTEG and TBSG had emission at 574 nm, while TTEG and TBSG had emission at 544 nm a new form of molecular interaction. The values were mean of 6 replicates and intensity increased as the concentration increased except at 1.5 mol% of TBSG which experienced fluorescence quenching.

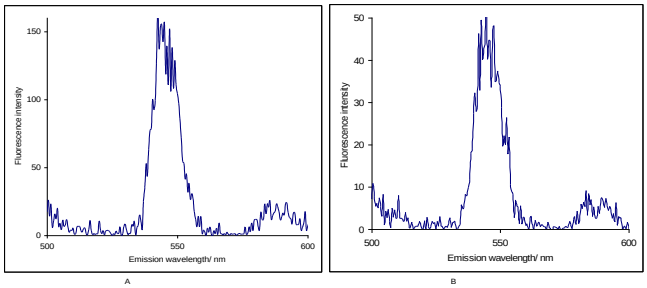

Fig. 4 2 mol% emission spectra of TBSG at (A) 483 nm and (B) 350 nm excitation wavelengths

Observation also showed that the fluorescence intensity for TTEG was low compared to DBSG, DTEG and TBSG and could be due to higher refractive index of the tellurite glass host [16] which has been observed to be greater than 1.95. Also the TTEG fluorescence intensity increases as the concentration increases until at it curved downwards at 2 mol% concentrations due to fluorescence quenching (Fig. 5).

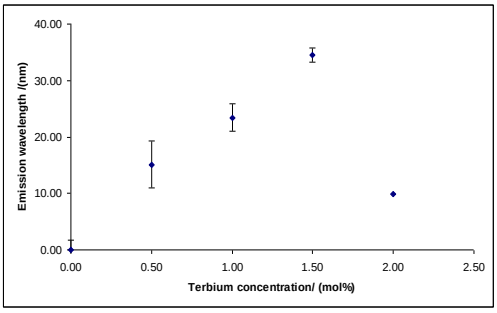

Fig. 5 Graph of emission wavelength against concentration of TBTEG at 484 nm

The absorption maximum of cyclohexane was 261 nm and fluorescence emission of cyclohexane was determined to be at 300 nm. Fluorescence characterization of crude oil was observed to give excitation at 219 nm and emission at 350 nm. They fluorescence characterization of DBSG and TBSG in cyclohexane shows both have fluorescence intensity increasing as concentration increases.

Crude oil characterization of DBSG at 1.5 mol% concentration experienced fluorescence quenching while TBSG tends to increase as the concentration increases. The variation in DTEG was evaluated using two way ANOVA with replication as shown in Table 1 below.

Table 1 Two way ANOVA with replication for DYTEG characterization in crude oil

Source of Variation	SS	df	MS	F	P-Value	F-Crit
Sample	122114.5	3	40704.85	24.13452	2E-07	3.008786
Columns	716.2092	5	143.2418	0.008493	0.993948	2.620652
Interaction	1637.569	15	109.1713	0.064729	0.999999	2.107676
Within	40477.96	24	1686.582			
Total	164946.3	47				

The results in Table 1 above confirms that in Fexp for samples at 24.13 was greater than Fcrit at 3.00 indicating that there was significant difference between the samples (451 nm and 481 nm). Also the Fexp for column interaction was less than Fcrit and therefore had no significant level of interaction, thus no sample interaction with the different days. In addition TTEG fluorescence characterization obtained did not conform to fluorescence characterization; a two way ANOVA test without replicate was performed to determine if the level of interaction within groups and among groups was significant with crude oil.

Table 2 Two way ANOVA without replication for TTEG characterization in crude oil

Source of Variation	SS	df	MS	F	P-Value	F crit
Rows	6736.657367	3	2245.552	135.07663	4.45E-11	3.28738281
Columns	45.15155	5	9.03031	0.5431999	0.7409763	2.9012952
Error	249.3642833	15	16.62429			
Total	7031.1732	23				

Thus from the above Table 2, since the value of F_{crit} at 3.287 between rows (concentration) was less than F_{exp} at 135.076, thus there was a significant difference between the different concentrations while F_{crit} at 2.901 between the columns (days) is greater than F_{exp} at 0.543, therefore there was no significant difference between the days thus the different days did not affect the analysis but samples only varied due to their different concentration.

4. Conclusion

Analysis by UV/VIS absorption spectrometer showed TBTEG as having only one excitation wavelength which indicates a different form of energy interaction that has a special ability to mask other excitation wavelength; this however did not make the dopant any less effective. The fluorescence characterization of the glass dopants typically showed signs of good prospects in the intended use. The boro-silicate glass matrix apparently enhanced its dopants light transmitting ability with higher intensity in both hosts; however the values obtained in tellurite glass dopants had more acceptable result with minimal deviation. The fluorescence determination of showed that DBSG was a compatible taggants with cyclohexane while the fluorescence determination of compatibility of taggants with crude oil identified TTEG as the ideal taggant having a higher precision with lower standard deviation than others.

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